

(19) **European Patent Office**

(11) **EP 1 088 809 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Disclosure date:
04/04/2001 Patent Gazette 2001/14

(51) Int. Class.⁷: **C07C 37/08, C07C 45/53**

(21) Application no.: **00117403.6**

(22) Application date: **08/11/2000**

(84) Contract states named:
**AT BE CH CY DE DK ES FI FR GB
GR IE IT LI LU MC NL PT SE**
Applicable states named:
AL LT LV MK RO SI

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(30) Priority: **09/30/1999 DE 19946888**

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Construction 1042-PB15
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(54) **A method for the preparation of phenol, acetone and methyl ethyl ketone**

(57) Phenol is most often prepared with a Hock separation of cumene hydro peroxide, in which case one naturally obtains equal molar parts of acetone as the joining product; however, there will be fewer application markets in the future for acetone than for phenol.

In accordance with the invention, phenol and acetone are prepared by oxidation of a mixture that contains cumene and up to 25% by weight sec-butyl benzene and with a following Hock separation of hydro peroxide and it is thus possible to control the ratio between the commercially valuable products phenol / acetone / methyl ethyl ketone by way of the composition of the educt mixture.

Preparation of phenol, acetone and methyl ethyl ketone.

Description

[0001] The invention concerns a method for the preparation of phenol, acetone and methyl ethyl ketone, in which is oxidized a mixture that contains cumene and sec-butyl benzene and this is followed by a Hock separation of cumene hydro peroxide and sec-butyl benzene hydro peroxide.

[0002] Phenol is an important chemical base material with many application possibilities. In addition to its application as a solvent, phenol can also be used for the preparation of phenol resins, bisphenol-A, ϵ -caprolactam, adipic acid, alkyl phenols and softeners.

[0003] A method is known for preparing phenol with a Hock separation of a suitable hydro peroxide. In addition to the phenol as the hydroxy compound, this process always produces a carbonyl product as joining product, for which one must also find a use for economical reasons.

[0004] Disclosure specifications EP-0 548 986 A1 describe a method for the preparation of phenol and methyl ethyl ketone (abbreviated MEK) as the joining product through oxidation of sec-butyl benzene to form sec-butyl benzene hydro peroxide and a subsequent Hock separation of the sec-butyl benzene hydro peroxide to form phenol and MEK. In addition to acetone, MEK is one of the technically most important ketones that is most often used as a lacquer and resin solvent. EP-0 548 986 A1 contains the proposal to have the starting material consist of sec-butyl benzene that is either basically free of ethyl hydro peroxide, carbonic acid and phenol or is basically free of styrene compounds or is basically free of methyl benzyl alcohol. Above all and by way of suitable processes that are adjusted for these materials and consist of special additional processing steps, an improved separation of undesirable secondary products is achieved. In that manner, it is possible to return unreacted sec-butyl benzene to the oxidation phase without creating negative effects for the oxidation velocity.

Disclosure specifications EP-0 578 194 A2 also concern a method for the preparation of phenol and MEK from sec-butyl benzene. The document describes a method, in which the conventional process phases of oxidation, concentration and separation are followed by special phases and particularly by an alkali wash of the MEK fraction that was separated by distillation and it is believed that this will increase the purity of MEK.

[0005] From US patent 4 532 360 is known a direct single-stage method that can also be used for the preparation of phenol and MEK from sec-butyl benzene. In that manner, the oxidation of the sec-butyl benzene is performed in the presence of hydrogen bromine or of hydrogen chloride as well as of at least one additive from the group cerium oxide, triphenyl borate, boron triphosphate and water, in which case direct separation of the sec-butyl benzene hydro peroxide to form phenol and MEK is achieved.

[0006] From patent document JP-62-114 922 of May 26, 1987 is known a method for the simultaneous preparation of phenol, MEK and acetone with oxidation of sec-butyl benzene with a gas containing molecular oxygen in the presence of cumene or cumene hydro peroxide. By adding 5 to 60% by weight of a cumene hydro peroxide concentration product that contains 65 to 85% by

weight cumene hydro peroxide to the sec-butyl benzene or by adding at least 50% by weight and ideally between 30 and 70% by weight cumene to the sec-butyl benzene, in which case value % by weight refers to the content of sec-butyl benzene, a higher reaction velocity for the oxidation of sec-butyl benzene is achieved. Furthermore, this reduces the dependence of the oxidation velocity of the sec-butyl benzene on the isobutyl benzene content and also reduces the formation of the secondary product acetophenone. Accordingly, the oxidation may be performed with a lesser cumene quantity when cumene is added to the sec-butyl benzene.

[0007] However, phenol is now most often prepared with a Hock separation of cumene hydro peroxide, in which case acetone is achieved as the joining product. Acetone also has many application possibilities, e.g., as a solvent or for the preparation of bisphenol-A and methyl methacrylate.

[0008] In this so-called cumene method for the preparation of phenol and acetone, cumene is oxidized first with preferably air or oxygen to form cumene hydro peroxide that is then - after a concentration phase with distillation by separating the unreacted cumene to reach a cumene hydro peroxide content of between 60 and 85% by weight - separated under an acid catalysis, preferably with sulfuric acid, to form phenol and acetone. A good overview of the cumene method can be found in Weissermel/Arpe, Industrial Organic Chemistry, Second Edition, Verlag Chemie, 1978, or in Ullman's Encyclopedia of Industrial Chemistry, Vol. A 19, Page 302 and following, VCH Verlagsgesellschaft 1991. Above all, new developments for the cumene method concentrate on the area of the cumene hydro peroxide separation and the processing of the separation product to reduce the formation of secondary products and the energy consumption; see, for example, EP-0 589 588 A1, EP-0 670 296 A1 or WO 97/06905.

[0009] In a molar manner, the cumene method always leads to equal parts for the preparation of phenol and acetone. In relation to the weight, 0.62 tons acetone per ton phenol is achieved. The bisphenol-A synthesis represents a major field of application for both products, in which case 1 mol bisphenol-A is obtained from 2 mol phenol and 1 mol acetone as a function of the reaction equation. Bisphenol-A is used as the starting material for the preparation of polycarbonates and epoxy resins and is thus produced in large quantities. However, and from a molar point of view, the acetone quantity required for the synthesis to form bisphenol-A is only one-half of the required phenol quantity. Although there exist other application possibilities for acetone such as solvents or the preparation of methyl methacrylate, for example, the prognosis points to a different market growth for phenol and acetone, i.e., there will be a greater demand for phenol than for acetone. However, and due to its reaction schematic, the cumene method used most often for the preparation of phenol and acetone will not meet the different market requirements.

[0010] Accordingly, one is faced with the task of developing a method for the preparation of phenol that also produces acetone, but does not produce it in the same manner as the cumene method, i.e., it does not produce equivalent molar quantities of phenol and acetone, but permits an economically sound flexible adjustment - from a molar point of view - to accommodate an expected and slightly higher demand for phenol than for acetone.

[0011] In accordance with the invention, this task is solved as indicated in patent claim 1 with a method for the preparation of phenol, acetone and methyl ethyl ketone that consists of the oxidation of a mixture that contains cumene and sec-butyl benzene with a gas containing molecular oxygen and consists of a subsequent separation of cumene hydro peroxide and sec-butyl benzene hydro peroxide and is characterized by the fact that the mixture containing cumene and sec-butyl benzene contains up to 25% by weight sec-butyl benzene. The mixture preferably consists only of cumene and sec-butyl benzene.

[0012] It was a surprise to find that method steps known from the cumene method can also be used to treat mixtures that simultaneously contain cumene and small quantities up to 25% by weight sec-butyl benzene and can be reacted together to form phenol, acetone and MEK. In this manner, adjusting the composition of the educt mixture makes it possible to control the phenol:acetone:MEK molar ratio in the product mixture in a targeted manner and to generally avoid an excess quantity of one of the two created carbonyl compounds that cannot be marketed. Accordingly, the method in accordance with the invention has the substantial advantage to adjust the production for the valuable products phenol, acetone and MEK to the market conditions, in which case it becomes particularly possible to avoid the predicted excess acetone capacity.

[0013] Since the mixture that contains the cumene and up to 25% by weight sec-butyl benzene in relation to the mixture can be reacted according to the invention and under the conditions known from the commonly used cumene methods, the method in accordance with the invention can also be realized in a fast and simple manner in existing units that operate using the cumene method. Regarding the realization in the area of oxidation and separation, one preferably tends to rely on existing units; an adjustment is required only for the educt supply and particularly for the processing of the separation product flows to produce the individual valuable products. Accordingly, it is easy to expand an existing production unit for phenol and acetone that operates on the basis of a conventional cumene method to make it suitable for the method in accordance with the invention or for an operation in accordance with the invention as a function of the market situation or for the preparation of only phenol and acetone.

[0014] Accordingly, the educt for the method in accordance with the invention consists of a mixture that - in addition to cumene and in accordance with the invention contains up to 25% by weight, preferably up to 20% by weight and particularly preferred between 10 and 20% by weight sec-butyl benzene. This mixture can be stored already in storage tanks or can be created by forming the mixture from different sources prior to being fed to the oxidation reactor. It is also possible to meter the material flows that contain cumene or sec-butyl benzene separately into the oxidation reactors and to mix them there.

[0015] In a preferred manner, the educt mixture in accordance with the invention is prepared directly for the oxidation phase by way of an alkylation of benzene with a corresponding mixture of propene and butene-1/butene-2 in the presence of a commercially available alkylation catalyst such as AlCl_3 , $\text{H}_3\text{PO}_4/\text{SiO}_2$ or zeolite. In that respect, the gas mixture containing propene, butene-1 and butene-2 can be obtained directly from a cracker, thus deleting an additional separation of the gas mixture into propene and butene-1/butene-2 for the separate preparation of cumene and sec-butyl benzene, for example.

[0016] The bubble column reactors known from the cumene method are considered the preferred oxidation reactors. Oxidation is performed as in the cumene method, preferably without catalyst, at temperatures of between 100 °C and 140 °C, at pressure values of 1 to 20 bar and in the presence of gas that contains air (preferable) or oxygen as molecular oxygen, until the oxidation has produced a peroxide content of up to 40% by weight in the product flow. The rest includes mainly unreacted cumene and sec-butyl benzene, since the cumene/sec-butyl benzene mixture is almost pure. Furthermore, the content also includes small quantities of some secondary products that were formed during the oxidation. This particularly refers to dimethyl phenyl carbinol, 2-phenyl butanol, acetophenone and propiophenone.

[0017] As is the case for the conventional cumene method, the product flow from the oxidation process can be fed directly or through an intermediate storage unit to a concentrating unit, in which the content of cumene hydro peroxide is increased to preferably 40 to 65% by weight and/or of sec-butyl benzene hydro peroxide is increased to preferably 5 to 15% by weight in the material flow, i.e., preferably by distillation in a vacuum by separating unreacted cumene and/or sec-butyl benzene.

Preferably after a further processing phase, the separated cumene and/or sec-butyl benzene is returned to the oxidation unit.

[0018] The material flow from the concentrating unit is now fed to the separation unit, where the catalysis is achieved preferably and in accordance with the invention with acid in the homogenous phase, i.e., preferably with sulfuric acid. The cumene hydro peroxide and sec-butyl benzene hydro peroxide are basically reacted here to form phenol, acetone and MEK. Suitable separation reactors and reaction conditions are known, for example, from EP-0 589 588 A1 and WO 97/06905. Analogous to the method described in these patent documents, it may be advantageous to expose the separation product to a post-tempering phase to reduce the content of undesirable secondary products that decrease the yield. To isolate the valuable products phenol, acetone and MEK, this is followed by a processing phase, preferably by distillation, for the separation product mixture in a manner that is known to the expert and is similar to the cumene method.

[0019] The method in accordance with the invention is not restricted to the main process steps listed here; it is indeed possible to also transfer all method variants known from the cumene method, supplements and circuits to the process method in accordance with the invention, i.e., particularly when they target a reduction of secondary products and an optimization of energy. With the knowledge of the method in accordance with the invention, many material processing and equipment-related design variants become accessible to the expert on the basis of the cumene method.

[0020] It is possible to achieve phenol, acetone and MEK separation yields of more than 90% with the method in accordance with the invention. With respect to its content of sec-butyl benzene, the composition of the educt mixture used for the oxidation is preferably adjusted such that sufficient marketing possibilities exist for the valuable products acetone and MEK that are obtained as joining products from phenol. In that manner, it will be possible to avoid an excess capacity and to achieve a high economic efficiency.

[0021] The process method in accordance with the invention will be explained in more detail with the following example, but is not restricted to it:

Example 1:

[0022] A mixture consisting of 80% by weight cumene and 20% by weight sec-butyl benzene is oxidized with oxygen at 132 °C in a bubble column reactor fitted with a thermostat. After an oxidation period of 2.5 hours, an analysis with a gas-phase-chromatograph (GC analysis) yielded a cumene hydro peroxide content of 21.5% by weight and a sec-butyl benzene hydro peroxide content of 2.9% by weight. This mixture is then exposed to a concentration phase under a high vacuum, in which case the analysis with gas-phase-chromatograph yielded 59.3% by weight cumene hydro peroxide and 8.1% by weight sec-butyl benzene hydro peroxide. The hydrocarbon mixture obtained as a distillate contains less than 1% peroxide calculated as cumene hydro peroxide. At a temperature of 50 °C, in a single-phase separation stage and in the presence of 2000 pm sulfuric acid, the hydrocarbon mixture obtained as a distillate is then dissolved in acetone or in a test separation product that consists of acetone, MEK, phenol and the hydrocarbon materials.

[0023] According to an evaluation of the analysis with a gas-phase-chromatograph, the separation yields were more than 95% for acetone, 92.3% for MEK and more than 99% for phenol.

Patent claims

1. A method for the preparation of phenol, acetone and methyl ethyl ketone carried-out with an oxidation of a mixture that contains cumene and sec-butyl benzene with a gas that contains molecular oxygen and with a subsequent Hook separation of cumene hydro peroxide and sec-butyl benzene hydro peroxide, characterized by the fact that the mixture that contains cumene and sec-butyl benzene contains up to 25% by weight sec-butyl benzene.
2. A method in accordance with claim 1, characterized by the fact that the mixture contains up to 20% by weight sec-butyl benzene.
3. A method in accordance with claim 2, characterized by the fact that the mixture contains between 10 and 20% by weight sec-butyl benzene.
4. A method in accordance with at least one of the previous claims, characterized by the fact that the mixture consists of cumene and sec-butyl benzene, both of which are of a high purity.
5. A method in accordance with at least one of the previous claims, characterized by the fact that the mixture is created on the basis of an alkylation of benzene with a gas mixture that contains propene, butene-1 and butene-2.
6. A method in accordance with at least one of the previous claims, characterized by the fact that the oxidation is performed with a gas that contains air or oxygen as molecular oxygen.

7. A method in accordance with at least one of the previous claims, characterized by the fact that the oxidation occurs at temperatures of between 100 °C and 140 °C.
8. A method in accordance with at least one of the previous claims, characterized by the fact that the oxidation product is concentrated by distillation prior to the separation by separating cumene or sec-butyl benzene.
9. A method in accordance with claim 8, characterized by the fact that the separated cumene or sec-butyl benzene or both are returned to the oxidation process.
10. A method in accordance with at least one of the previous claims, characterized by the fact that the separation mixture is homogenous.
11. A method in accordance with at least one of the previous claims, characterized by the fact that the separation is obtained with an acid catalysis.
12. A method in accordance with claim 11, characterized by the fact that sulfuric acid serves as the acid.

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EUROPEAN SEARCH REPORT

Application number
EP 00 11 7403

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| <p style="text-align: center;">RELEVANT DOCUMENTS</p> | | | |
| Category | Designation of the document with indication of the relevant passage, where required | Relevant claim number | CLASSIFICATION OF THE APPLICATION (Int. Class.7) |
| X, D | <p>PATENT ABSTRACTS OF JAPAN Vol. 011, No. 326 (C-454) October 23, 1987 (1987-10-23) & JP 62 114922 A (DAINIPPON INK & CHEM INC), May 26, 1987 (1987-05-26) * Summary *</p> <p style="text-align: center;">-----</p> | 1-12 | <p>C07C37/08 C07C45/53</p> |
| <p>This search report was prepared for all patent claims</p> | | | <p>SEARCHED AREAS (Int. Class.7) C07C</p> |
| Search location MUNICH | Completed on: December 21, 2000 | Prepared by: Janus, S. | |
| <p>CATEGORY OF THE LISTED DOCUMENTS</p> | | | |
| <p>X: Of particular significance when considered alone. D: Document listed in the application.</p> | | | |

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**APPENDIX TO THE EUROPEAN SEARCH REPORT
FOR THE EUROPEAN PATENT APPLICATION NO.**

EP 00 11 7403

This appendix indicates the members of the patent families relating to the patent documents listed in the above-mentioned European search report.

The information given about the family members represents the status of the data file maintained at the European Patent Office as of 12/21/2000.

These data are given for information only and there is no guarantee.

| Patent document listed in the search report | Publication date | Member of the patent family | Publication date |
|------------------------------------------------|-------------------|--------------------------------|------------------|
| JP 62114922 A | 05/26/1987 | NONE | |

See Official Gazette No. 12/82 of the European Patent Office for more detailed information for this appendix.